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FOREIGN TECHNOLOGY DIVISION

SEMICONDUCTOR PROPERTIES OF ORGANIC DYES

1. PHTHALOCYANINES

by

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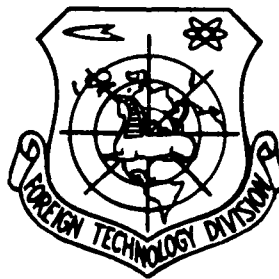
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М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere.
When written as ё in Russian, transliterate as yё or ё.

RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English	Russian	English	Russian	English
sin	sin	sh	sinh	arc sh	$\sinh^{-1}$
cos	cos	ch	cosh	arc ch	$\cosh^{-1}$
tg	tan	th	tanh	arc th	$\tanh^{-1}$
ctg	cot	cth	coth	arc cth	$\coth^{-1}$
sec	sec	sch	sech	arc sch	sech^{-1}
cosec	csc	csch	csch	arc csch	csch^{-1}

Russian	English
rot	curl
lg	log

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SEMICONDUCTOR PROPERTIES OF ORGANIC DYES.

1. PHTHALOCYANINES.

A. T. Vartanyan.

A new class of synthetic dyes is phthalocyanine, systematically investigated by Linstead together with coworkers [1, 2], is of great interest not only in connection with their application as dyes, but also for biochemistry in form of its close structural resemblance to porphyrins, which generate base for many important natural pigments (hemoglobin, chlorophyll)[1].

FOOTNOTE[1]. Porphine is the fundamental structural nucleus of chlorophyll and hemoglobin. This compound consists of four rings of pyrrole, in all α-positions connected by methine groups. ENDFOOTNOTE.

However, Linstead proposed the structural formula of phthalocyanine, schematically depicted in Fig. 1a. The correctness of this structure was confirmed by the investigations of Robertson [3] with the aid of X-rays. Hydrogen atoms within the 16-member ring are not fixed/recorded in the separate atoms of nitrogen, but they are arranged in such a way that each of them simultaneously belongs to two atoms of nitrogen.

Because of this interatomic distance of nitrogen, connected with

hydrogen bridges, it is less (2.65 Å), than between same, not connected with atoms of hydrogen (2.76 Å). For the purpose of the complete agreement of the structural formula of phthalocyanine with the results of chemical and physical investigations, Endermann [4] somewhat modifies the formula of Linstead, assuming within the 16-member ring the existence of not hydrogen atoms, but protons and electrons. In this case both the protons and the electrons are located at the different ends/leads of the 16-member ring (Fig. 1b). With the formation of complex salt of metal from the free phthalocyanine the twice positively charged ion of metal connects both electrons and because of this it becomes atom.

Molecules of phthalocyanine and its complex salt possess a flat/plane structure. Phthalocyanines of some metals (for example, copper and of magnesium) are centrally symmetrical. Hence it follows that the atoms of these metals lie/rest at that plane, that also four atoms of nitrogen, and coordinatively tetravalent atoms of copper and magnesium are evenly held by four atoms of nitrogen (Fig. 1c). Supplementary valency forces within the 16-member ring add exceptional stability to complex salts.

In the 16-member ring all bonds of identical length (1.34±0.03 Å), alternation of single and double bonds cannot be revealed/detected. Consequently, the large ring of phthalocyanine and its derivatives is a resonance hybrid. This representation is confirmed also by such facts as the diamagnetic crystalline anisotropy

of phthalocyanine [5] and the discrete spectrum of absorption [6-10].

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Phthalocyanines are characterized by unusual resistance to heating and light. Many of them can be sublimated at a temperature of 500-600°. They are isolated also by their stability to the chemical effects. These pigments actually do not undergo in air of oxidizing destruction.

From other remarkable properties of phthalocyanines there should be mentioned their catalytic properties, for example, the conversion of parahydrogen into normal [11, 12]. Cook [13] discovered that phthalocyanine of iron possesses the same catalytic properties as hemin and other containing iron compounds of the group of porphyrin. Cook and also Helberger and Heaver [14] found that phthalocyanines of magnesium and zinc at 180° are approximately oxidized by organic peroxides with the emission of clear red light (chemiluminescence). Analogous phenomena were observed, also, in the case of other macrocyclic pigments, which contain magnesium and zinc, for example, of chlorophyll [15, 16]. fluorescence is phthalocyanine in the solutions/openings it observed Yevstigneev [17].

Since electrical properties of phthalocyanines are not yet studied, also, in our previous investigations [18] this class of dye-pigments was not included, we, taking into account a number of their remarkable properties, decided to extend the investigations also to some representatives of this class of dyes.
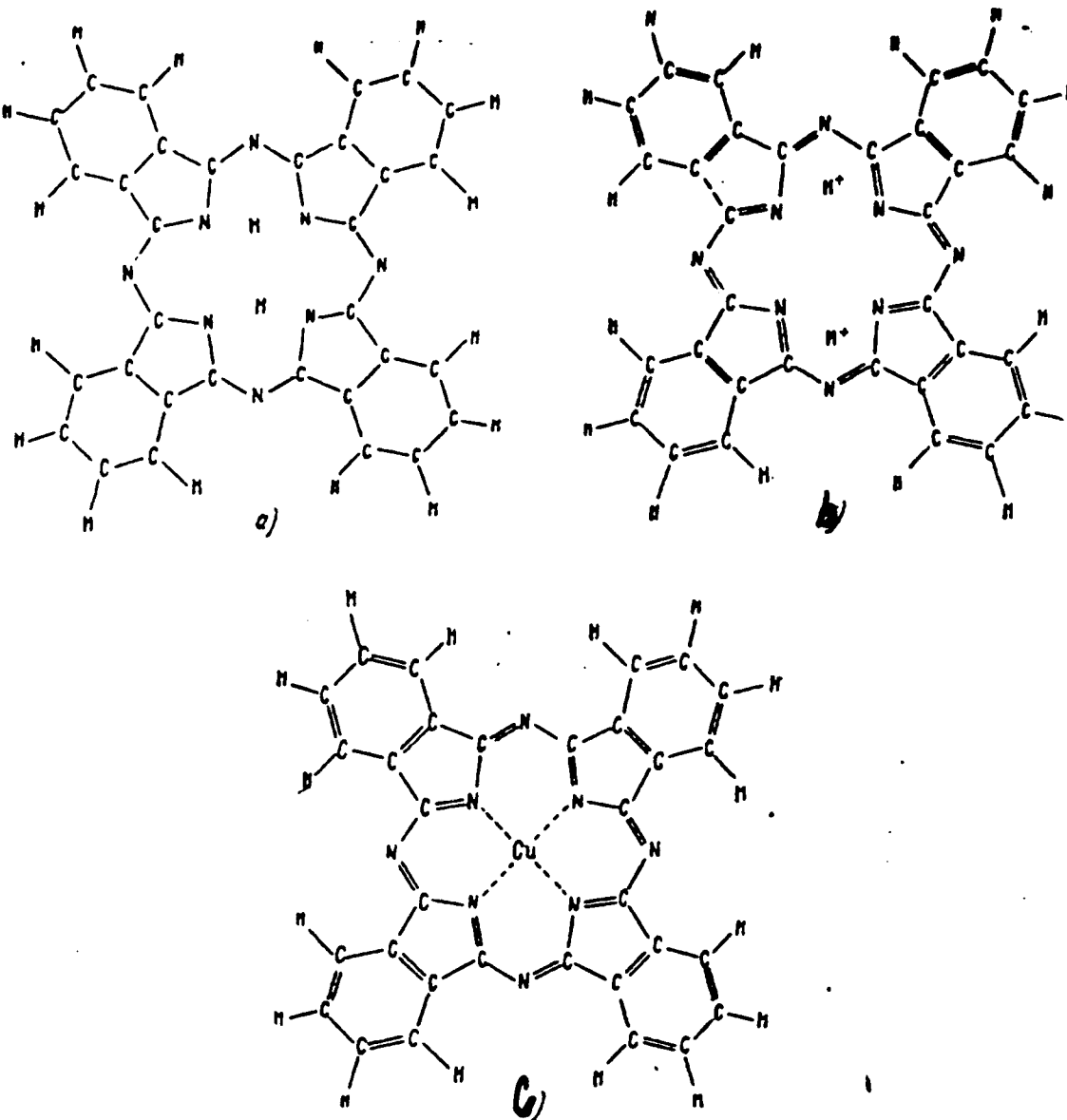
Fig. 1. a) structural formula of phthalocyanine according to Linstead; b) the same, according to Endermann; c) structural formula of phthalocyanine of copper.

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Given in this article are results of the investigation of the

volt-ampere dependence, and also the effect of heating and oxygen on the electroconductivity.

EXPERIMENTAL PART.

1. Description of installation.

Installation on which there was studied electroconductivity of phthalocyanine is analogous in which the photoconductivity of thin layers of dyes was previously investigated, and which is described in detail in the preceding article [18].

Essential part of the installation is a thin-walled quartz "finger", on the lower part of which there are applied by cathode sputtering two gold electrodes at a distance of 0.5 mm from each other. The length of electrodes is equal to 10 mm. Quartz finger/pin was inserted by means of the section into the glass container, connected with the high- vacuum installation. This design of the instrument made it possible to observe in the vacuum and in an atmosphere of extraneous gas in the temperature interval from -180° to +200°C.

Light currents were measured by mirror galvanometer of Hartman and Brown with a sensitivity of $6.3 \cdot 10^{-10}$ A with the distance of the scale from mirror of 4 m. Voltage was measured by a voltmeter of class 0.5.

Oxygen was gotten from potassium permanganate and to intake into reaction container for several hours was maintained/withstood at temperature of liquified air.

2. Investigated objects.

Investigated were: phthalocyanine (without metal), phthalocyanines of copper and magnesium and water-soluble sulfonated phthalocyanine. The first three objects were chemical, pure, and the latter - technical[1].

FOOTNOTE[1]. Objects were kindly furnished by the laboratory of photo-biochemistry of the Institute of Biochemistry of the Academy of Sciences of the USSR. ENDFOOTNOTE.

Since the first three dyes in the usual solvents (water, alcohol, ether/ester, benzene, etc.) are not dissolved, the method of coating used by us previously, which consists of the rapid deposition of dye of the evaporating solution/opening, here could not be applied. Therefore, with exception of the sulfonated phthalocyanine, layers were deposited to the quartz surface by the pulverization of the dye between the gold electrodes. These dye-pigments sufficiently solidly attach to the quartz, and easily can be obtained uniform transparent layers with the selective reflection, characteristic for crystalline state. In the case of the sulfonated phthalocyanine the layers were obtained by the deposition of dye from the evaporating aqueous

solution.

Investigated layers had thickness on the order of 10-20 μ.

3. Results.

All the phthalocyanines investigated by us possess noticeable dark conductivity. Since depending on the duration of the effect of the field, the duration of aging of the layer in the vacuum at high temperatures and the presence of extraneous gas the conductivity of layer can undergo more or less considerable changes, then it cannot be stated about the specific conductivity of the phthalocyanines and about the physical constant. Nevertheless, for purposes of orientation we give (see the Table) the values of the resistances of the layers investigated by us, and also the "specific" conductivities of phthalocyanines for the fresh (aged up to one hour at 100°) layers under vacuum conditions.

Resistance of the layer and "specific" conductivity of

phthalocyanines.

(1) Краситель	(2) Сопротивле- ние слоя в омах	(3) «Удельная» проводимость в ом⁻¹ см⁻¹
Фталоцианины (без металла) (4)	1,5·10¹⁰	6,7·10⁻⁸
Фталоцианин меди (5)	2,0·10¹⁰	5,0· ⁻⁸
Фталоцианин магния (6)	7,0·10⁸	1,4· ⁻⁶
Фталоцианин сульфированный (7)	1,0·10¹⁰	10,0·10⁻⁸

Key: (1). Dye. (2). Resistance of the layer in ohms. (3).

"Specific" conductivity in $\Omega^{-1} \cdot cm^{-1}$. (4). Phthalocyanines (without

metal). (5). Phthalocyanine of copper. (6). Phthalocyanine of

magnesium. (7). Phthalocyanine, sulfonated.

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It is evident from the table that with the exception of

phthalocyanine of magnesium, the "specific" conductivity of other

investigated phthalocyanines has an approximately identical order.

The "Specific" conductivity of phthalocyanine of magnesium at least by

one order is higher than the remaining. Below we will show that

phthalocyanine of magnesium by other properties is isolated among

other of phthalocyanines.

Fig. 2 shows change in current strength, passing through layer of

phthalocyanine of copper, in dependence on time of heating in vacuum

at 100°, in continuous pumping out and constantly applied field. From

the figure one can see that even in 10 hours. aging in the vacuum

layer finally was not stabilized. Conductivity change at room

temperature completely can be disregarded after the prolonged aging of

layer in the vacuum at 100°. At a temperature in 100° measurements, which require into whole not more than one hour, also can be produced without taking into account a change in the resistance with time.

One should also note that the electroconductivity of sulfonated phthalocyanine greatly depends on whether the field is applied to the layer or not. If we disconnect the field, then the original conductivity is reached only after a certain time. In the constantly applied field the conductivity, although slowing down, continuously it increases.

4. Dependence of current strength on field strength.

Since the dependence of current strength on field strength have investigated we not only in vacuum, but also in the atmosphere of oxygen, and since presence of oxygen in certain cases affects value of electroconductivity, before presenting results of present paragraph, we will give short characteristic of effect of oxygen on electroconductivity; in detail effect of oxygen will be examined into § 5.

a) phthalocyanine (without metal). At room temperature the presence of oxygen under the pressure in several hundred millimeters Hg does not affect the electroconductivity of phthalocyanine. Prolonged heating at 100° and illumination in the atmosphere of oxygen also do not cause any considerable changes.

b) phthalocyanine of copper. At room temperature the

phthalocyanine of copper behaves analogously with phthalocyanine without the metal, but if we in the presence of oxygen heat or to illuminate the layer of phthalocyanine of copper, then its electroconductivity sharply grows/rises. With the simultaneous illumination and during the heating the conductivity can increase into dozens of times.

c) phthalocyanine of magnesium. In contrast to the previous dyes, the electroconductivity of phthalocyanine of magnesium in the presence of oxygen grows/rises already at room temperature. Heating layer in the presence of oxygen leads to an increase of the conductivity into hundreds of times.

d) sulfonated phthalocyanine. As in the case of free from the metal of phthalocyanine, at room temperature the presence of oxygen does not affect the electroconductivity of this dye. Heating and illumination in the presence of oxygen also strongly does not affect the conductivity of the sulfonated phthalocyanine.
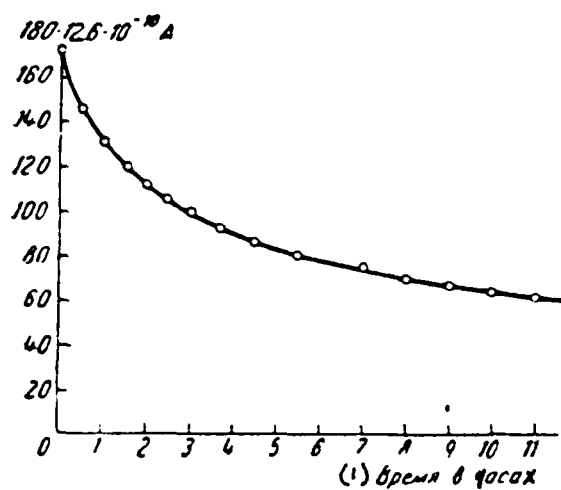
Fig. 2. Change in the strength of current passing through a layer of phthalocyanine of copper, depending on the time of heating in a vacuum.
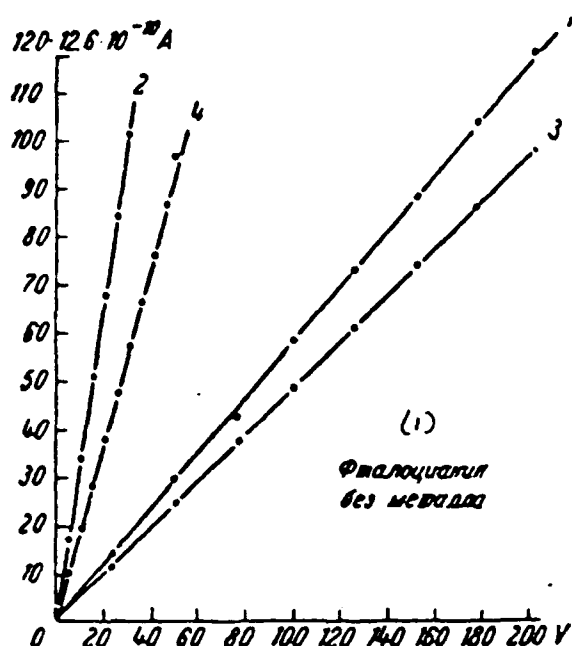
Key: (1). Time in hours.

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Fig. 3.   Fig. 4.

Fig. 3. Volt-ampere characteristic of phthalocyanine: 1 - in vacuum at 22° (value of current strength they are increased 10 times); 2 - in vacuum at 100°; 3 - in the atmosphere of oxygen (p=460 mm) at 68°; 4 - in the atmosphere of oxygen (p=460 mm) at 100°.

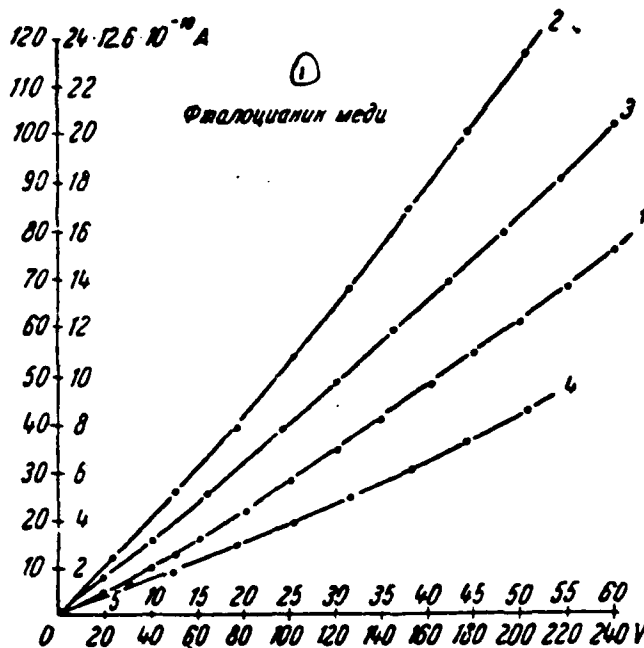Key: (1). Phthalocyanine without the metal.

Fig. 4. Volt-ampere characteristic of phthalocyanine of copper in vacuum: 1, 2 - at 100° (scale - left and lower); 3 - at 100° (scale - right and upper); 4 - at 20° (scale - right and lower).
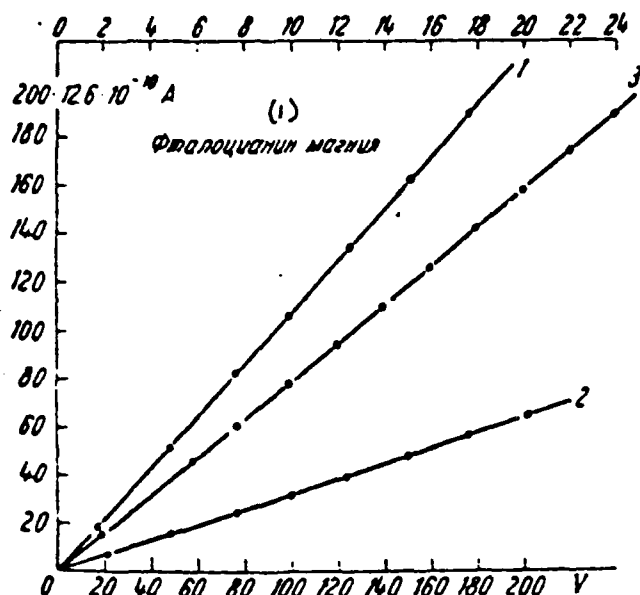
Key: (1). Phthalocyanine of copper.

Fig. 5.   Fig. 6.

Fig. 5. Volt-ampere characteristic of phthalocyanine of magnesium:

1, 2 - in vacuum at 20° (lower school); 3 - in the atmosphere of

oxygen (p=320 mm) at 20° (upper scale).

Key: (1). Phthalocyanine of magnesium.
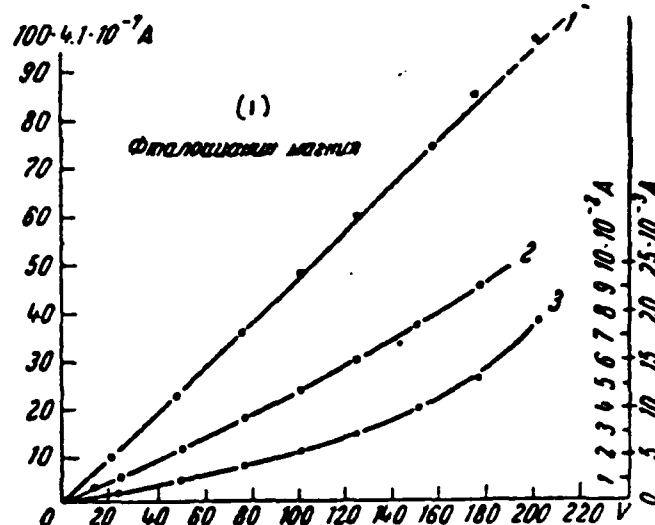
Fig. 6. Volt-ampere characteristic of phthalocyanine of magnesium

after the processing of the layer by oxygen (p=320 mm) at 100°. 1 -

for 1 hour; the temperature of layer of 22° (scale 10^{-7} A); 2 - during

2 hours; the temperature of layer of 100° (scale of $10p^{-3}$ A); 3 -

during 4 hours; the temperature of layer of 100° (scale 10^{-2} A).

Key: (1). Phthalocyanine of magnesium.

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For phthalocyanine the dependence of current strength on voltage

is shown in Fig. 3-7.

In Fig. 3. it is evident that with a field strength of up to 3000 V/cm Ohm's law in the case of the phthalocyanine is fulfilled with an accuracy of up to 2-3%. However, in the case of phthalocyanine of copper (Fig. 4) considerable divergences in the direction of a more rapid increase in current strength are observed. At room temperature these divergences become especially noticeable with the fields strength of above 500 V/cm. For the phthalocyanine of magnesium Ohm's law is fulfilled well both in a vacuum and in an atmosphere of oxygen, if only in the latter case layer did not undergo the prolonged heating (Fig. 5); otherwise very strong divergence from the linear dependence is observed (Fig. 6). For the sulfonated phthalocyanine obtaining volt-ampere characteristic presents considerable difficulties, since its conductivity in the constantly applied field, although slowing down, nevertheless continuously it increases. Therefore the points, obtained with the consecutive increase and the decrease of the field strength, lie down on the different curves (hysteresis). In these measurements the uncertainty with respect to the moment of reading is contained. Only these difficulties can to a certain degree be removed after prolonged aging in the vacuum at 100°. The obtained curves are shown in Fig. 7. Readings were taken after at this intensity there was not observed during five minutes a noticeable increase in current. In the case of the sulfonated phthalocyanine the divergence from Ohm's law is also observed.

5. Dependence of electroconductivity on temperature.

In the overwhelming majority of cases electroconductivity of phthalocyanines it was investigated in temperature interval from 0° to 100°, while sometimes layers tested in range from - with 80° to +200°. Lower than -100° electroconductivity of layers was so small at temperatures that by our instrument it could not be reliable measured.

All investigated phthalocyanines have positive temperature coefficient of conductivity (Fig. 8-12). For the phthalocyanine the characteristically almost complete coincidence of the curves, obtained in the vacuum and in the atmosphere of oxygen (Fig. 8).

Fig. 9 gives curves, obtained for phthalocyanine of copper in vacuum and in the atmosphere of oxygen, after multihour heating at 100°. For convenience in the comparison of results in each experiment the voltage was taken by such so that the divergence at 100° would be to entire scale of galvanometer.
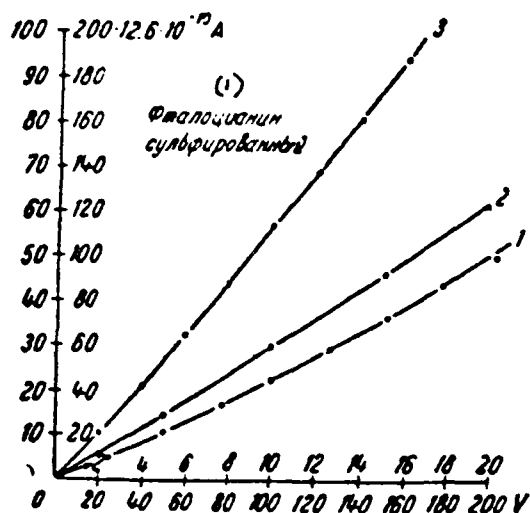
Fig. 7. Volt-ampere characteristic of sulfonated phthalocyanine: 1 -
in vacuum at 22° (scale - left and lower); 2 - in vacuum at 100°
(scale - right and upper); 3 - in the atmosphere of oxygen (p=260 mm)
at 100° (scale - right and upper).

Key: (1). Phthalocyanine, sulfonated.

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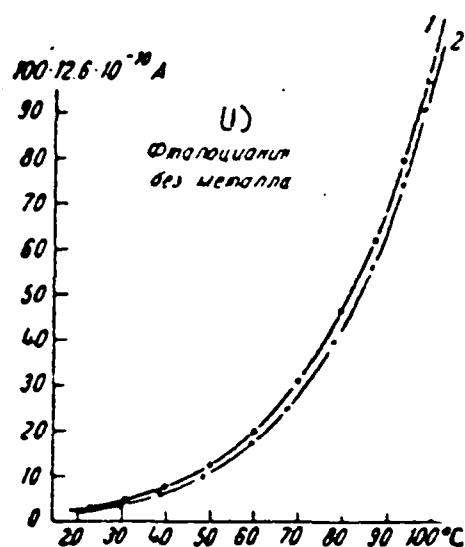Fig. 8.   Fig. 9.

Fig. 8.   Change in electroconductivity of phthalocyanine during

heating: 1 - in vacuum; 2 - layer during 2 hours were located in the

atmosphere of oxygen (p=460 mm) at 100°.
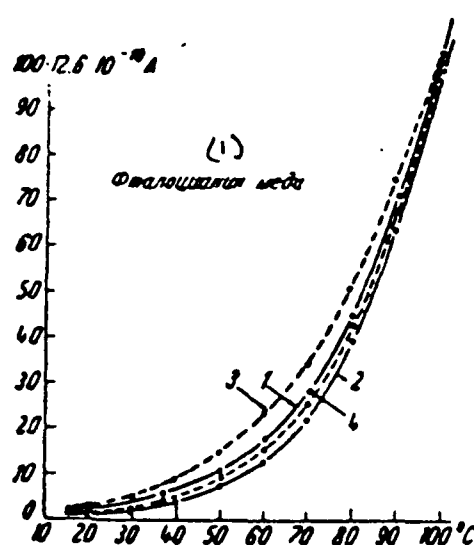
Key: (1). Phthalocyanine without the metal.

Fig. 9.   Change in electroconductivity of phthalocyanine of copper

during heating: 1 - layer during 4 hours was aged in a vacuum at

100°; voltage 70 V; 2 - layer during 17 hours were aged in a vacuum at

100°; voltage 250 V; 3 - layer during 12 hours were located in the

atmosphere of oxygen (p=240 mm) at 100°; voltage 35 V; 4 - layer after

pumping out of oxygen during 3 hours were aged in vacuum at 100°;

voltage 200 V.

Key: (1). Phthalocyanine of copper.

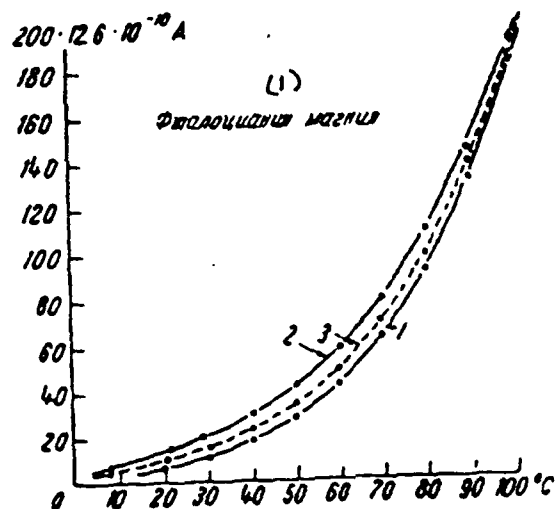Fig. 10. Change in electroconductivity of phthalocyanine of magnesium during heating: 1 - layer during 90 min. was aged in vacuum at 100°; voltage 12 V; 2 - layer during hour. it was located in the atmosphere of oxygen (p=10 mm) at 100°; voltage 1 V; 3 - layer, after the pumping out of oxygen during 4 hours, it was aged in a vacuum at 100°; voltage 2.4 V.

Key: (1). Phthalocyanine of magnesium.

Fig. 11. Change in electroconductivity of phthalocyanine of magnesium during heating: 1 - layer during 3 hours was aged in vacuum at 100°; voltage 22 V (left scale); 2 - during 1 hour. it was located in the atmosphere of oxygen (p=320 mm) at 100°; voltage 0.25 V; 3 - layer after the pumping out of oxygen during 20 hour. It was aged in a vacuum at 100°; voltage 19 V (right scale).
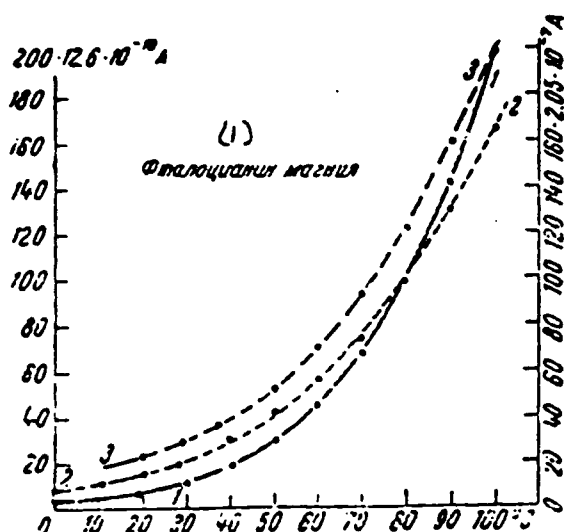
Key: (1). Phthalocyanine of magnesium.

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All four curves belong to the same layer. Its resistance is increased in proportion to aging of the layer in a vacuum. Despite the fact that points of curves 1 and 2 almost coincide at 100°, as a whole curve 1 is located above curve 2. Curve 3 relates to the layer processed by oxygen. It is located above curve 1. The pumping out of the oxygen and the subsequent treatment of layer in the vacuum at 100° leads to an increase in the resistance and reduction in entire curve (curve 4). The latter is arranged/located below even curve 1.

In the case of phthalocyanine of magnesium it is expedient to distinguish behavior of this dye at pressures of oxygen on the order of 10 mm and into several hundred millimeters.

It is evident from Fig. 10 that at low oxygen pressures the phthalocyanine of magnesium behaves analogously with phthalocyanine of copper. At the large oxygen pressures the phthalocyanine of magnesium undergoes the irreversible changes (Fig. 11).

It is evident from this figure that, first of all, curve 2 intersects curve 1 and, in the second place, curve 3 by nature is nearer to curve 2 than to curve 1.

Fig. 12 shows a change in the current strength during heating of layer of sulfonated phthalocyanine. As can be seen from the figure, the presence of oxygen in this case, as in the case of phthalocyanine (without the metal), it has little effect on the general/common shape of the curve. However, should be noted the intersection of curves 1

and 2; moreover their mutual arrangement is opposite to the arrangement of the analogous curves of phthalocyanine of magnesium (Fig. 11, curves 1 and 2). The curve obtained after the pumping out of oxygen and subsequent treatment of the layer in a vacuum at 100° almost completely coincides with curve 1, and Fig. 12 does not show it.

PROCESSING AND DISCUSSION OF THE RESULTS.

As is known, the dependence of electroconductivity of semiconductors on temperature is expressed by the Van't Hoff formula:

$$\sigma = A\ e^{-\frac{U}{2kT}},$$

where U – dissociation energy of electron (or hole). According to this formula, between lg σ and 1/T must exist linear dependence. Determining the angular coefficients of straight lines, we find U. If admixtures/impurities introduce supplementary levels, then should be expected change in constant U.

This construction is made on the basis of data of Fig. 8-12. Results are given in Fig. 13-16[1].

FOOTNOTE[1]. In Fig. 13-16 along the axis of ordinates the values of the logarithm of the value, proportional to conductivity, are plotted. ENDFOOTNOTE.

We see that in all cases the linear dependence between lg σ and 1/T is

confirmed sufficiently well in the wide temperature interval.

It is evident from Fig. 13 that in the case of phthalocyanine both in a vacuum and in an atmosphere of oxygen by pressure in 460 mm straight lines have almost identical inclination/slope. It appears from this that the presence of oxygen barely influences the value of energy of the electron detachment in the phthalocyanine. The calculated from the inclination/slope of straight lines constant U on the average is equal to 0.87 eV. But if we consider the insignificant effect of oxygen, then its presence leads to an increase in value of U for 0.03 eV (U=0.9 eV).
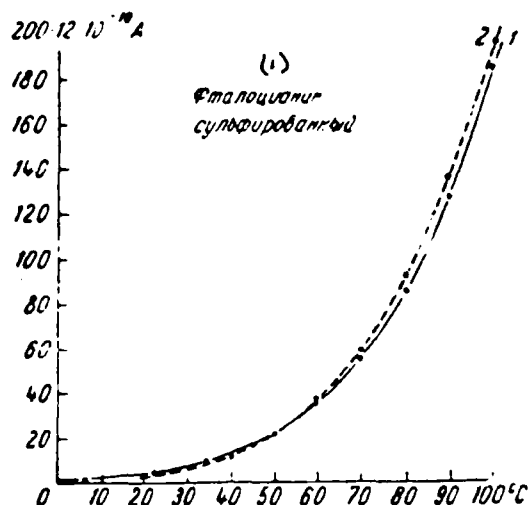
Fig. 12. Change in electroconductivity of sulfonated phthalocyanine during heating: 1 - layer during 2 hour. It was aged in the vacuum at 100°; voltage 50 V; 2 - layer during illegible hour were located in the atmosphere of oxygen (p=22 mm) at 100°; voltage 50 V.

Key: (1). Phthalocyanine sulfonated.

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In contrast to phthalocyanine, energy of electron detachment in phthalocyanine of copper depends on quantity of sorbed oxygen (Fig. 14). In proportion to the removal/distance of oxygen from the layer energy U increases, approximately, from 0.9 eV (straight line 1) to 1.1 eV (straight line 2). During the most complete removal/distance of oxygen energy U was equal to 1.2 eV. Under the effect of oxygen energy U falls to 0.82 eV (straight line 3). In this case the linear dependence lg σ in the function 1/T was checked in the temperature interval from -30° to 100°. Intense illumination (3500 luxes), apparently somewhat accelerates the process, which causes decrease of

u, and after 3 hour. illumination at a temperature of layer of 100°
energy U became equal to 0.77 eV (straight line 4). After the pumping
out of oxygen and aging of layer in the vacuum during 3 hours at 100°
energy U increased from 0.77 eV to 1.0 eV (straight line 5).

It must be noted that illumination not only contributes to rapid
decrease of U in presence of oxygen, but also to its rapid increase
with pumping out. The effect of light is apparently reduced to the
supplementary heating of the layer. Thus, in the case of
phthalocyanine of copper we deal with a reversible process, which is
reduced to the formation of the compound, which easily decomposes
during the heating in a vacuum.

A decrease in energy U, discovered for phthalocyanine of copper
as a result of processing layer by oxygen, is more distinctly
developed in the case of phthalocyanine of magnesium. For the fresh
layer of phthalocyanine of magnesium in the vacuum energy U is equal
to 0.78 eV (Fig. 15, line 1). The presence'of oxygen at room
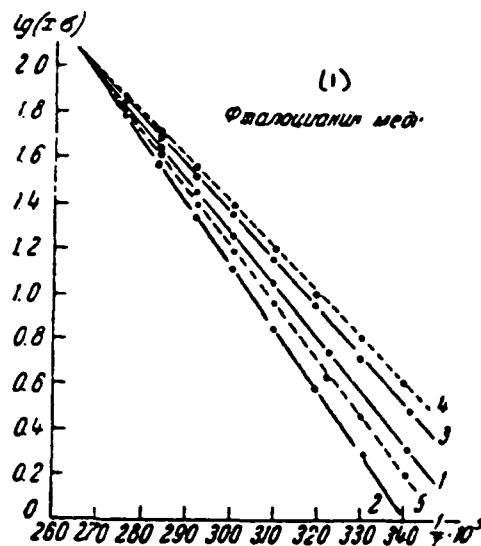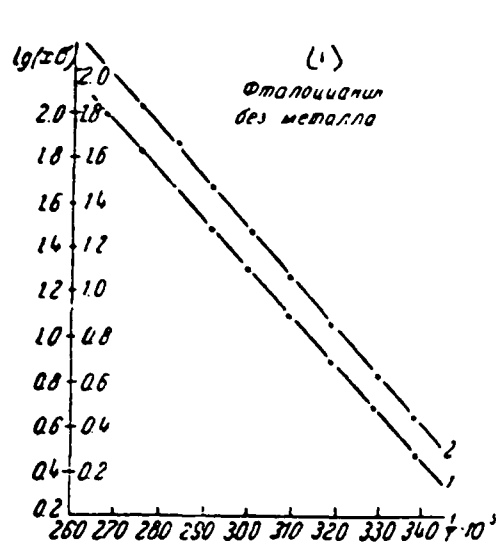temperature causes the increase of conductivity.

Fig. 13.   Fig. 14.

Fig. 13. Dependence of lg (xσ) in function
1/T: 1 - vacuum (left scale); 2 - in an atmosphere of oxygen

(p=460 mm, right scale).

Key: (1). Phthalocyanine without metal.

Fig. 14. Dependence of lg (xσ) in function 1/T: 1 - in vacuum after

4 hours of pumping out at 100°; 2 - in vacuum after 17 hours of

pumping out at 100°; 3 - in the atmosphere of oxygen (p=420 mm) after

12 hours of heating at 100°; 4 - in an atmosphere of oxygen (p=420 mm)

after 12 hours of heating at 100° and 3 hours of illumination by tube

to 2000 W; 5 - in vacuum after pumping out of oxygen and aging in

vacuum at 100° for 3 hours.

Key: (1). Phthalocyanine of copper.

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However, this process to a greater degree is reversible. Heating

layer in the presence of oxygen (p~10 mm) leads to a considerable

decrease in energy U. From the slope of line 2 it is determined at 0.62 eV. The subsequent pumping out of oxygen and the prolonged aging of layer in the vacuum at 100° leads to the partial reduction (U=0.72 eV) previous conductivity (straight line 3). In the atmosphere of oxygen by pressure in 320 mm energy U falls to 0.47 eV (straight line 5). The subsequent pumping out and the prolonged aging of layer lead to a small increase in energy U (0.53 eV, straight line 6).

It is impossible to get rid of the effect of oxygen, even if the aging of the layer is conducted in vacuum at 200°. Energy U as before remains within limits of 0.5 eV. If during 10 hours the layer in the atmosphere of oxygen (p=260 mm) is heated at 185°, then the energy U falls to value 0.40-0.42 eV and in the subsequent aging in the vacuum energy U is not increased. Thus, at high temperatures phthalocyanine of magnesium in an irreversible manner interacts with oxygen.

A decrease in energy U in the presence of oxygen can be detected also at temperatures lower than 100°. Thus, for instance, if the layer of phthalocyanine of magnesium during 10 hours is heated in air at 60°, then under the vacuum conditions energy U, instead of 0.78 eV, proves to be equal to 0.52 eV. In order to reveal/detect the effect of oxygen at room temperature, the layer of phthalocyanine of magnesium after the pumping out of air and aging of layer in the vacuum during 3 days was sustained in the atmosphere of oxygen (p=260 mm) at 20°, and then was determined energy U in the temperature interval from - 30 to +20°. In this case was obtained value of 0.68

eV, instead of 0.78 eV in the vacuum. The totality of these facts leads to the conclusion that in the case of phthalocyanine of magnesium energy U is very sensitive to oxygen. These, apparently should be explained the anomalously high "specific" conductivity of phthalocyanine of magnesium, given in the table (S 3).
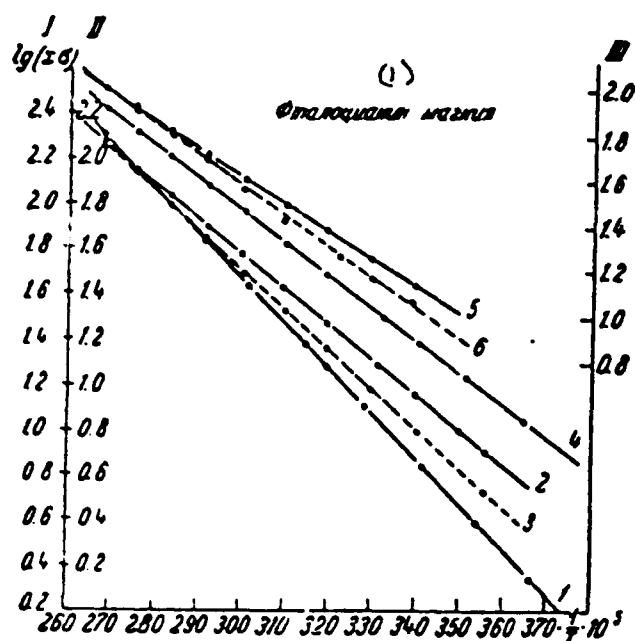
Fig. 15. Dependence of lg (xσ) in function 1/T: 1 - in vacuum after 3 hours of pumping out at 100° (scale 1); 2 - in the atmosphere of oxygen (p=10 mm after 2 hours of heating at 100° (scale 1); 3 - in vacuum after pumping out of oxygen (p=10 mm and aging of the layer in vacuum at 100° during 4 hours (scale 1); 4 - in the atmosphere of oxygen (p=320 mm), after 1 hours of heating at 100° (scale II); 5 - in the atmosphere of oxygen (p=320 mm) after 5 hour. heating at 100° (scale III); 6 - in the vacuum after pumping out (p=320 mm) and aging in the vacuum at 100° during 20 hour. (scale III).
Key: (1). Phthalocyanine of magnesium.

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In a vacuum for sulfonated phthalocyanine the energy is equal to 0.9 eV (Fig. 16, line 1). After treatment of layer by oxygen energy U is increased to 0.92 eV (line 2). The pumping out of oxygen and aging

layer in the vacuum leads to the decrease of energy U to 0.87 eB (line 3). Consequently, the sulfonated phthalocyanine behaves analogously with free phthalocyanine.

Investigated phthalocyanines can be broken into three groups: 1) phthalocyanines, whose energy U, in as a result of the reaction of the dye with oxygen, changes insignificantly (0.03 eV) and besides in direction of its increase (phthalocyanine and sulfonated phthalocyanine); 2(phthalocyanines, whose change in energy U carries reversible character (phthalocyanine of copper); 3) phthalocyanines, for which a change in energy U has an irreversible character (phthalocyanine of magnesium). It is interesting that between the phthalocyanines, depending on the nature of the atom of metal, the explicit chemical differences emerge: Linstead [2] distinguishes the stable covalent coordination compounds, from which the metal does not yield to removal without the destruction of entire complex (for example, phthalocyanine of copper) and labile covalent coordination compounds, from which the metal comparatively easily can be distant by acids (for example, phthalocyanine of magnesium).

Since oxygen barely influences value of energy U of phthalocyanine, we assume that change of energy in the case of phthalocyanines of copper and magnesium it is caused by reaction of oxygen with atoms of metal. In view of the fact that the layers investigated by us undoubtedly have microcrystalline structure, the increase of energy U to 0.03 eV in the case of phthalocyanine and

sulfonated phthalocyanine is most natural to ascribe to the effect/action of oxygen in the gaps between the separate microcrystal particles. Therefore, the possibility is not excluded that also in the case of phthalocyanines of copper and magnesium occurs an analogous increase in energy U on the order of 0.03 eV, but it is suppressed by stronger decrease as a result of the reaction of oxygen with the atoms of metal. The investigation of the behavior of porphyrazine (Fig. 17) in the presence of oxygen would aid resolution to the question: is there caused an increase in energy U of phthalocyanine by the reaction of oxygen with the central 16-member ring or with the periphery of the molecule? Unfortunately, attempts at the synthesis of porphyrazine were unsuccessful [19].

The possibility of the strong connection of oxygen with phthalocyanine of magnesium and irreversibility described above connected with it are in accordance with chemiluminescence, which was being observed during heating of phthalocyanine of magnesium (and also compounds of magnesium of other dyes of type of porphyrin) with peroxide of Tetralin [14]. In this case it is assumed that in the first phase the central atom of metal is driven out by oxygen of peroxide in the form of oxide.
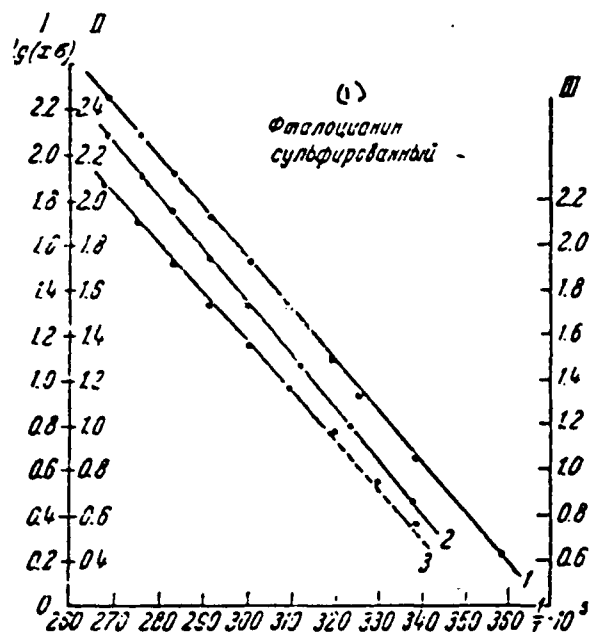
Fig. 16. Dependence of lg (xσ) in function 1/T: 1 - in vacuum (scale I); 2 - in the atmosphere of oxygen (p=260 mm); after 2 hours of heating at ᴎ00° (scale II); 3 - in vacuum after pumping out of oxygen and aging of layer in vacuum at 100° for 2 hours (scale III). Key: (1). Phthalocyanine, sulfonated.

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During heating of phthalocyanine (without the metal) and phthalocyanine of copper with commercial Tetralin chemiluminescence was not observed, and only during the heating with peroxide of Tetralin was observed very weak glow. However, the section of the dye free from the metal seems doubtful. It is possible that in the latter case it is caused by traces of metallic complexes, from which it is very difficult to be freed. In the opinion of Linstead [7], by this pollution/contamination it is possible to explain the maximum of

absorption in the phthalocyanine (without the metal) when λ=6750 Å, measured by Stern and Pruckner [6], but not discovered in the measurements of Linstead.

As is known, chlorophyll intensely fluoresces by saturated red light. However, the substitution of magnesium in the chlorophyll with copper leads to a dye incapable of fluorescence and photo-sensitization. The introduction of copper or silver into hematoporphyrin also leads to the nonfluroescing compounds, while the introduction of zinc gives fluorescent compounds. All these facts are in accordance with works through the chemiluminescence and are caused by processes of the transfer of electrons. The high sensitivity of energy U of phthalocyanine of magnesium to oxygen suggests about its connection/communication with the exceptional role of magnesium in the natural coloring substances of the type of chlorophyll.

Possibility of penetration of oxygen between crystal planes of phthalocyanine follows from measurements of Robertson. On the investigations of latter [3] of plane of the adjacent molecules of phthalocyanine it is almost perpendicular. Identical molecules are isolated by intervals into 4.72 Å; moreover the perpendicular distance between the parallel molecules is equal to 3.38 Å; it is almost equal to the distance between the layers in graphite (3.41 Å). Since the diameter of the molecule of oxygen on the order of 3 Å [20], then, obviously, oxygen can penetrate inside the crystal and be connected to the atoms of metal, forming thus either the oxygen bridges between the

molecules or compounds of the type of peroxides[1].

FOOTNOTE[1]. Something analogous occurs during the bloating of graphite as a result of the penetration of liquid, and also oxygen between crystal planes [21]. ENDFOOTNOTE.

It is possible, however, that oxygen operates on the metal, which is present in the dye in the form of admixture/impurity.

In number of cases Ohm's law is fulfilled with an accuracy to 2-3% (Fig. 3.5). But are observed completely explicit divergences (Fig. 4, 6, 7). In the case of phthalocyanine of magnesium (Fig. 6) these divergences are caused by liberation of Joule heat, since with the same strengths of field (3000 V/cm), but under small current strengths the volt-ampere characteristic of phthalocyanine of magnesium is expressed by straight line (Fig. 5).

As a result of reaction of layer with oxygen energy U so decreases that power of current with strengths of field on the order of 3000 V/cm (Fig. 6, curve 3) reaches value of several watts. It is clear that under these conditions for observing the temperature constancy of layer it is necessary to take supplementary measures. The Joule heat isolating in the layer will heat layer, in consequence of which the current strength even more will increase. Process will be continued until heat liberation and heat emission are counterbalanced. Knowing the temperature dependence of

electroconductivity, it is possible to rate/estimate an increase in temperature (Δt) as a result of the liberation of Joule heat. With the fields strength into 2000-3000 V/cm det for curve 2 (Fig. 6) has the value of the order of several degrees.
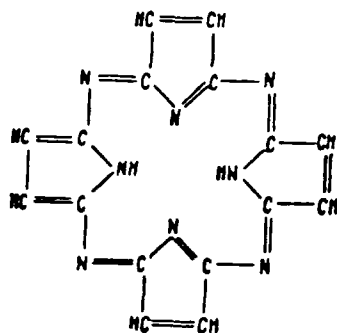
Fig. 17. Structural formula of porphyazine.

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In the case of phthalocyanine of copper a divergence from Ohm's law is observed already at small power of current. In order in this case to explain divergence, it is necessary to additionally assume that its thermal conductivity is less than the thermal conductivity other of those investigated of phthalocyanines. Corresponding data are absent. However, below we will see that the results of tests on the effect of light for the conductivity of phthalocyanine of copper also must be explained by the assumption of smaller thermal conductivity than in the case of other phthalocyanines.

As regards the sulfonated phthalocyanine, then in this case divergences from Ohm's law cannot be explained only by the liberation of Joule heat, since its conductivity depends also on the duration of the applied field. This behavior of the sulfonated phthalocyanine, possibly, should be explained by the insufficient cleanliness of object.

It remains t is to examine question about photosensitivity of layers of phthalocyanines. With exception of phthalocyanine of copper, the conductivity of other of phthalocyanines with the illumination by the visible and ultraviolet radiation it does not undergo considerable changes. The observing increase of conductivity completely can be explained by heating layer as a result of luminous absorption. Corresponding calculations, based on the knowledge of energy U, and also direct measurements of the temperature difference, which leads to the observed increase in the conductivity, completely coincide; with the illumination of layer in 5000 luxes an increase in the temperature of the layer of altogether only of 1-2°.

In the case of phthalocyanine of copper increase of conductivity under the effect of visible light is considerably more than in the case of other of phthalocyanines. In order to cause the appropriate increase in the conductivity by heating, the temperature of layer must be increased on 15-20°. In spite of considerable temperature difference, we must consider that as in this case the discussion is not about photoconductivity, but about heating of the layer as a result of low thermal conductivity of the layer, as this was assumed during the explanation of volt- ampere characteristic.

Convincing us in this are also speeds of the establishment of the maximum conductivity with illumination and drops of conductivity during the disconnection of light.

For the detection of photoconductivity, apparently a highly sensitive installation is necessary.

Further work is devoted to the explanation of question of nature and mechanism of conductivity of phthalocyanines.

CONCLUSIONS.

1. There was measured in a vacuum the dark conductivity of thin layers of phthalocyanine in solid state. The "specific" conductivity of phthalocyanine (without metal), phthalocyanine of copper and sulfonated phthalocyanine of one order, on the average of $5 \cdot 10^{-8} \ \Omega^{-1}$ cm^{-1}. The "specific" conductivity of phthalocyanine of magnesium is, approximately, $10^{-6} \ ohm^{-1} cm^{-1}$.

2. There are obtained volt-ampere characteristics both in a vacuum and in the atmosphere of oxygen. The divergences from Ohm's law, observed in certain cases, are assigned to the effect of heating as a result of the liberation of Joule heat.

3. There was investigated the conductivity change of phthalocyanines during heating. It is shown that in a certain temperature interval the electroconductivity is expressed by exponential law. Energies of the electron detachment are calculated.

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4. Effect of oxygen on conductivity of layers of phthalocyanine was investigated. In the case of phthalocyanines of copper and magnesium, there is discovered the considerable decrease of energy of the electron detachment. However, in the case of phthalocyanine (without the metal) and sulfonated phthalocyanine the presence of oxygen in the layer leads to a small increase in the energy of the electron detachment.

5. Are shown semiconductor properties of phthalocyanines.

6. Conductivity changes under the effect of visible and ultraviolet radiation was not discovered. The observing increase of conductivity with the illumination is caused by heating layer as a result of luminous absorption.

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